DOCUMENT RESUME

ED 025 101 EF 001 892

By- McClelland, Nina I.

Water Quality Considerations and Related Dishwashing Problems.

National Sanitation Foundation, Ann Arbor, Mich.
Pub Date Nov 65
Note- 32p.
EDRS Price MF-$0.25 HC-$1.70
Descriptors- *Cleaning, Disease Control, *Dishwashing, Health Needs, Public Health, *Sanitation, *Water Resources

A number of the chemical and physical factors which cause dishwashing problems are presented in a series of charts. Water quality considerations are vital, but the importance of good housekeeping and proper operating practices cannot and must not be minimized. Topics discussed include--(1) dissolved minerals, (2) dissolved gases, (3) detergents, and (4) appendix. (RH)

WATER QUALITY CONSIDERATIONS

AND

RELATED DISHWASHING PROBLEMS

Nina I. McClelland

ED025101

U.S. DEPARTMENT OF HEALTH, EDUCATION & WELFARE
OFFICE OF EDUCATION

THIS DOCUMENT HAS BEEN REPRODUCED EXACTLY AS RECEIVED FROM THE PERSON OR ORGANIZATION ORIGINATING IT. POINTS OF VIEW OR OPINIONS STATED DO NOT NECESSARILY REPRESENT OFFICIAL OFFICE OF EDUCATION POSITION OR POLICY.

EF 001892

Published

By

The National Sanitation Foundation

ED025101

WATER QUALITY CONSIDERATIONS AND RELATED DISHWASHING PROBLEMS

by

Nina I. McClelland*

Of all the chemical substances with which we've come into contact, water is the one which all of us have the greatest tendency to take for granted. It arouses little curiosity, yet it has a number of very unique properties:

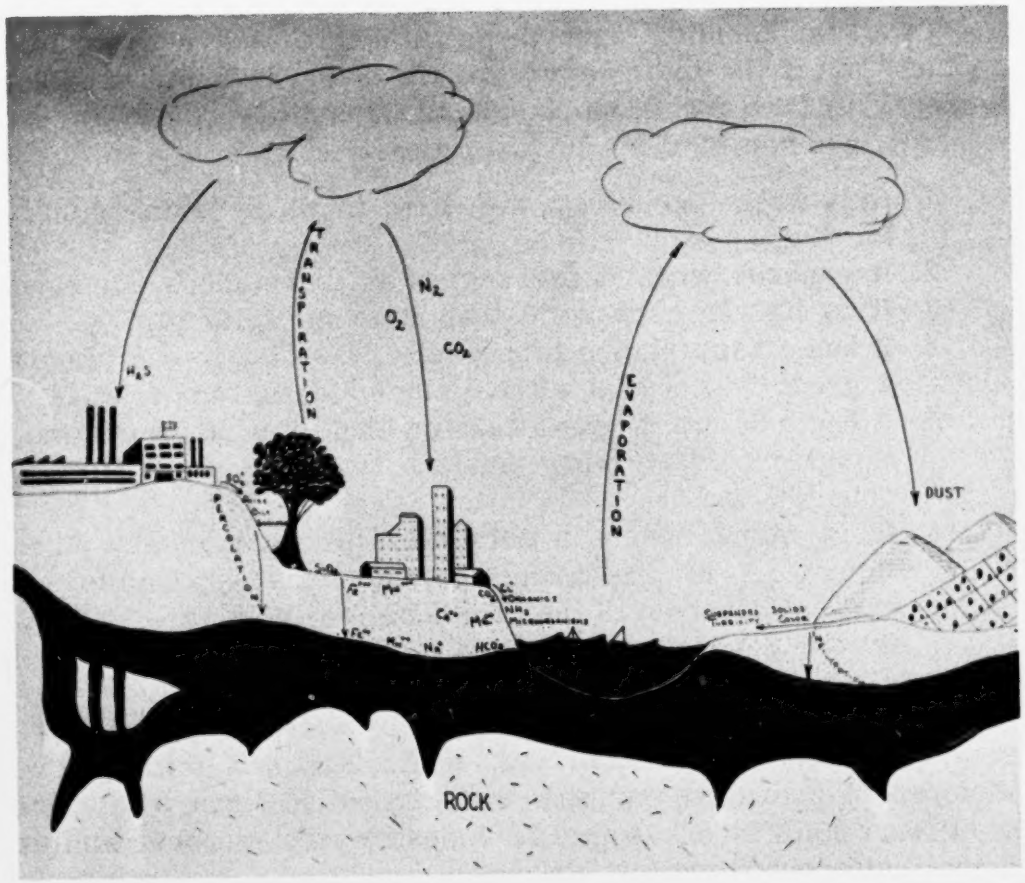
1. Only water occurs on the earth in three forms simultaneously,
2. It expands when it freezes; most substances contract,
3. It is lighter as a solid than it is as a liquid,
4. It has a very high heat capacity; that is, it can absorb a great deal of heat without much rise in temperature,
5. It has a higher surface tension than any other common liquid except mercury (surface tension = the ability to cohere), and
6. It is more nearly a universal solvent than any other liquid. It is this property which is responsible for many if not most of the problems we must face in conditioning water for our use.

Although the chemical structure of water is still represented as "H_2O", we know that deuterium and tritium, two isotopes of hydrogen, combine with oxygen to form a mixture of at least 33 different isomers. Indeed water is not a simple compound about which all is known.

In the complex society which we know today, there is virtually no such thing as "pure" natural water. In being a superior solvent, any form of precipitation collects air contaminants as it falls to the ground. These include suspended

*Presented at Dishwashing NAFEM Industry Meeting, New York City, on Saturday, November 6, 1965.

solids (dust), atmospheric gases (including air "pollutants"), and microorganisms. A schematic illustration of how the quality of water changes as it moves through the hydrologic cycle is shown in Figure 1. Some of the water which falls to the earth is immediately returned to the atmosphere through the processes of evaporation and transpiration. Others run over the land, collecting street washings, eroding soil, and other waste materials, which it carries with it to the collecting lakes and streams. Still more percolates through the soil, dissolving minerals as it goes.



Key:

1,2, & 3 - Air pollutants and atmospheric gases
4 - Transpiration
5 - Evaporation
6 - Percolation
7 - Industrial wastes
8 - Domestic wastes
9 - Land erosion and farm runoff

Figure 1: Schematic Illustration of Hydrologic Cycle

Because of the day to day and seasonal variations in mineral content, turbidity, and temperature, river water generally requires the largest treatment facilities. The beneficial effect of self-purification by sedimentation usually makes the quality of water drawn from lakes, ponds, or impoundment reservoirs superior to that drawn from a flowing stream. Because of the filtering action of the soil, ground water—particularly that drawn from a deep well—is usually free from turbidity and pathogenic bacteria. It is also quite consistent in terms of quality and temperature, but it has acquired carbon dioxide from the atmosphere and from decaying organic matter, making it a weak carbonic acid. This increases its power as a solvent, so its mineral content is often high.

The current estimate of industrial water usage in the United States is 130 billion gallons per day. Less than one-tenth of this is purchased from municipalities. Surface supplies are used for 91%, and ground water furnishes the other 9%.

In general, the following impurities can be considered to have industrial significance:

1. Dissolved minerals
2. Dissolved gases.
3. Free mineral acid acidity
4. Oils and greases
5. Turbidity and sediment
6. Color and organic matter
7. Tastes and odors
8. Microorganisms

DISSOLVED MINERALS

Hardness

Calcium (Ca^{++}) and magnesium (Mg^{++}), which are commonly referred to as "the hardness-causing irons," are the most universal constituents of natural water. For industrial purposes, they are among the most important considerations. Hardness is responsible for scale depositions, for excessive soap consumption, and for the formation of undesirable films, scums, and curds.

Calcium carbonate ($CaCO_3$) is the salt most commonly found in scale. It may be deposited at temperatures even less than 150^{o} F. At every temperature, an equilibrium exists

DISSOLVED MINERALS

Hardness Ions	Source	Potential Problems	Removal Methods
Calcium (Ca^{++}) and Magnesium (Mg^{++})	Rocks	Scale formation Excessive soap consumption Formation of films, scums, and curds	Lime-soda softening Cation exchange Sodium Zeolite Hydrogen Zeolite Demineralization Distillation May be retained in solution by internal conditioning

between free carbon dioxide (CO_2) in the water and the amount of calcium bicarbonate ($Ca(HCO_3)_2$) which can be held in solution. At times, even slight elevations in temperature are sufficient to upset this equilibrium. The break-down of calcium bicarbonate or magnesium bicarbonate ($Mg(HCO_3)_2$) to form scale occurs according to the following reactions:

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2\uparrow$$

$$MgCO_3 \downarrow + H_2O \rightarrow Mg(OH)_2 + CO_2\uparrow$$

Two types of hardness are reported, carbonate (formerly called "temporary hardness") which is due to calcium and magnesium bicarbonates and carbonates, and non-carbonate (formerly called "permanent hardness") which is due to calcium and magnesium sulfates, chlorides, and nitrates.

The quantitative classification of hardness should be defined by each individual user to fit his particular need, but the following scheme is used by the U.S. Geological Survey:

mg/1 as $CaCO_3$	
0 - 60	Soft
61 - 120	Moderately hard
121 - 180	Hard
over 180	Very hard

The analytical results obtained in water analysis may be expressed in a variety of terms. In this country, these most commonly include:

1. parts per million (ppm)
   A unit weight of solute per million weight units of solution.

2. milligrams per liter (mg/l)
   Essentially the same as ppm in dilute solutions with density approximately equal to 1.

3. equivalents per million (epm)
   A unit chemical equivalent weight of solute per million weight units of solution

4. grains per gallon (gpg)
   The number of grains of solute per 1 U.S. gallon of water.

1 grain = 1/7000 lb.

1 U.S. gallon = 8.33 lbs.

1 gpg = 17.1 ppm.

In aqueous solution, almost all soluble salts exist in ionic form. Only weak acids, weak bases, the salts of weak acids or weak bases, and dissolved gases may be present in an un-ionized state. Expressing the results of a water analysis in terms of hypothetical salt concentrations is a convenience rather than a correct representation of the ionic state of the solutes. Nevertheless, hardness, alkalinity, and acidity are commonly reported as equivalent amounts of $CaCO_3$.

For example:

1 epm Mg = 12 ppm Mg = 42 ppm $MgCO_3$,
which would be reported as 50 ppm $CaCO_3$.

All acceptable water analyses are performed in accordance with the current edition of *Standard Methods for the Examination of Water and Wastewater*.

Removal of Hardness

For waters containing more than 100-150 mg/l hardness as $CaCO_3$, lime-soda softening usually provides the most suitable and the most economical treatment method.

1. Lime precipitates all the carbonate hardness according to the following reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

Magnesium non-carbonate hardness is also precipitated by the lime, but soluble by-products are produced, which add to the calcium non-carbonate hardness content:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4$$

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$$

2. Non-carbonate calcium hardness requires soda ash (sodium carbonate) for removal:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$$

Notice that in the reactions in which lime removes the carbonate hardness, the total solids content of the water is also reduced. This is not true, however, with soda ash and the non-carbonate hardness. Therefore, if the hardness of a given water supply is primarily carbonate, the total solids will be reduced in the lime softening process; but if the hardness exists primarily in the non-carbonate form, no appreciable reduction in solids can be expected with this form of treatment.

Softening by precipitation has little value with raw waters which contain less initial hardness than 50 - 100 mg/l. Under these conditions, an ion exchange process is often used for softening.

Zeolites are insoluble solid materials which have the ability to exchange certain of their ions for other ions with which they come into contact. Sodium zeolite is by far the most common of the ion exchange processes used in water conditioning. This resin - natural or synthetic - consists of a complex molecule with sodium ions attached. It exchanges the sodium for all ions with two or more positive charges.

$$\underset{(\text{or } Mg^{++})}{Ca^{++}} + \underset{\text{Sodium Zeolite}}{Na_2Z} \rightarrow \underset{\text{Calcium Zeolite}}{CaZ} + 2Na^+$$

These units ultimately lose their efficiency and must be regenerated with brine.

$$\underset{\text{(or MgZ)}}{CaZ} + 2NaCl \longrightarrow Na_2Z + \underset{\text{(wasted)}}{CaCl_2}$$

Figure 2 shows a schematic illustration of this process.

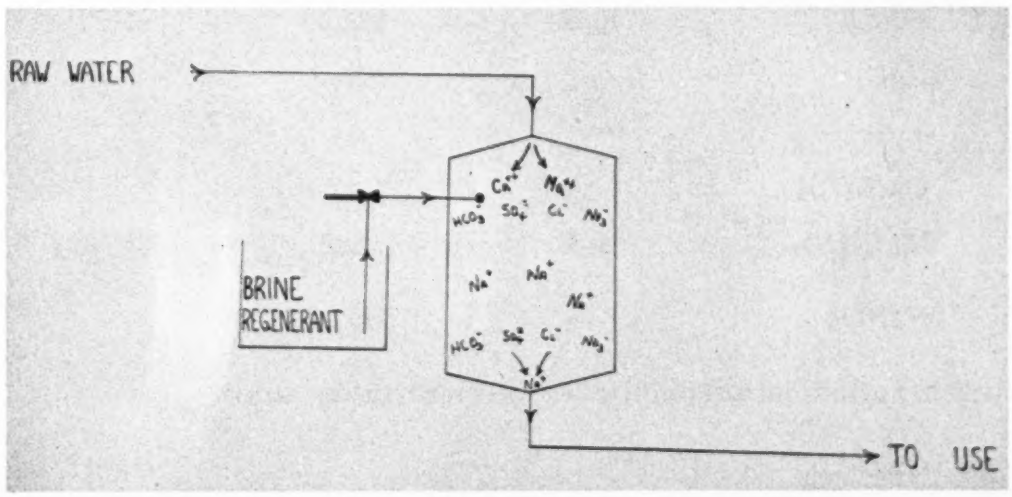


Figure 2: Schematic Illustration of Sodium Zeolite Ion Exchange Process

The hardness is reduced to - or nearly to - zero with sodium zeolite softening, but there are a number of limitations to its use:

1. The influent water should have a turbidity of less than 10 units, and must be free of ferric iron.
2. No reduction of alkalinity or total solids accompanies the removal of hardness.
3. The effluent water is normally corrosive because of the dissolved gases which are present.

Hydrogen zeolite exchange resins have the capacity to exchange hydrogen ions for other cations present. This converts the anions to their respective acids:

$$\begin{matrix} Ca(HCO_3)_2 & & & & CaZ & & \\ Mg(HCO_3)_2 & + & H_2Z & \longrightarrow & MgZ & + & 2H_2CO_3 \\ 2NaHCO_3 & & & & Na_2Z & & \end{matrix}$$

$$\begin{matrix} CaSO_4 \\ MgSO_4 \\ Na_2SO_4 \end{matrix} + H_2Z \longrightarrow \begin{matrix} CaZ \\ MgZ \\ Na_2Z \end{matrix} + H_2SO_4$$

$$\begin{matrix} CaCl_2 \\ MgCl_2 \\ 2NaCl \end{matrix} + H_2Z \longrightarrow \begin{matrix} CaZ \\ MgZ \\ Na_2Z \end{matrix} + 2HCl$$

$$\begin{matrix} Ca(NO_3)_2 \\ Mg(NO_3)_2 \\ 2NaNO_3 \end{matrix} + H_2Z \longrightarrow \begin{matrix} CaZ \\ MgZ \\ Na_2Z \end{matrix} + 2HNO_3$$

Regeneration is accomplished with sulfuric acid:

$$\begin{matrix} CaZ \\ MgZ \\ Na_2Z \end{matrix} + H_2SO_4 \longrightarrow H_2Z + \begin{matrix} CaSO_4 \\ MgSO_4 \\ Na_2SO_4 \end{matrix}$$

The carbonic acid produced from bicarbonates is unstable in aqueous solution and can be removed by aeration or by degasification. Thus hydrogen zeolite treatment not only removes all the hardness ions, but it also removes the bicarbonate alkalinity and reduces the total solids.

This process is most useful for waters which are low in hardness and high in bicarbonate alkalinity. One of its limitations is that the acid effluent must be neutralized in order to avoid corrosion. This may be accomplished by:

1. Running hydrogen and sodium zeolite units in parallel, feeding them in such a way as to obtain the desired alkalinity in the mixed effluent,
2. Neutralizing the effluent with an alkali, or
3. Diluting the effluent with raw, unsoftened water.

Demineralization is a combination of two ion exchange processes:

1. Hydrogen ion exchange for removal of cations, and

2. Anion exchange for the removal of anions.

An organic resin with sulfonic acid as the active group is frequently used for the cation exchange process:

$$\underset{\substack{\text{Hydrogen}\\\text{exchange}\\\text{resin}}}{R\cdot SO_3H} + NaCl \longrightarrow \underset{\substack{\text{Sodium}\\\text{resin}}}{R\cdot SO_3Na} + HCl$$

$$2R\cdot SO_3H + CaSO_4 \longrightarrow \underset{\substack{\text{Calcium}\\\text{resin}}}{(R\cdot SO_3)_2Ca} + H_2SO_4$$

Anion exchange resins are organic compounds with active amine or quaternary amine groups. Weakly basic resins remove only the anions of strong acids:

$$\underset{\substack{\text{Weakly basic}\\\text{exchange resin}}}{RNH_3\cdot OH} + HCl \longrightarrow \underset{\substack{\text{Chloride}\\\text{resin}}}{RNH_3\cdot Cl} + H_2O$$

Strongly basic resins remove the anions of both strong and weak acids. Silica acts as the anion of a weak acid. To remove silica, sulfide, or CO_2, strongly basic resins must be used.

$$\underset{\substack{\text{Strongly basic}\\\text{exchange resin}}}{R_4N\cdot OH} + \underset{\substack{\text{Silicic}\\\text{acid}}}{H_2SiO_3} \longrightarrow \underset{\substack{\text{Silicate}\\\text{resin}}}{R_4N\cdot HSiO_3} + H_2O$$

Influent water for demineralization must be free of suspended solids and organic matter. Figure 3 is a schematic illustration of this process.

The quality of demineralized or distilled water is expressed in terms of specific conductance. One micromho (μmho) of specific conductance (Λ) is generally considered to indicate a dissolved solids content of 0.5-0.6 mg/l. The low solids content of laboratory demineralized and distilled water is compared in Figure 4.

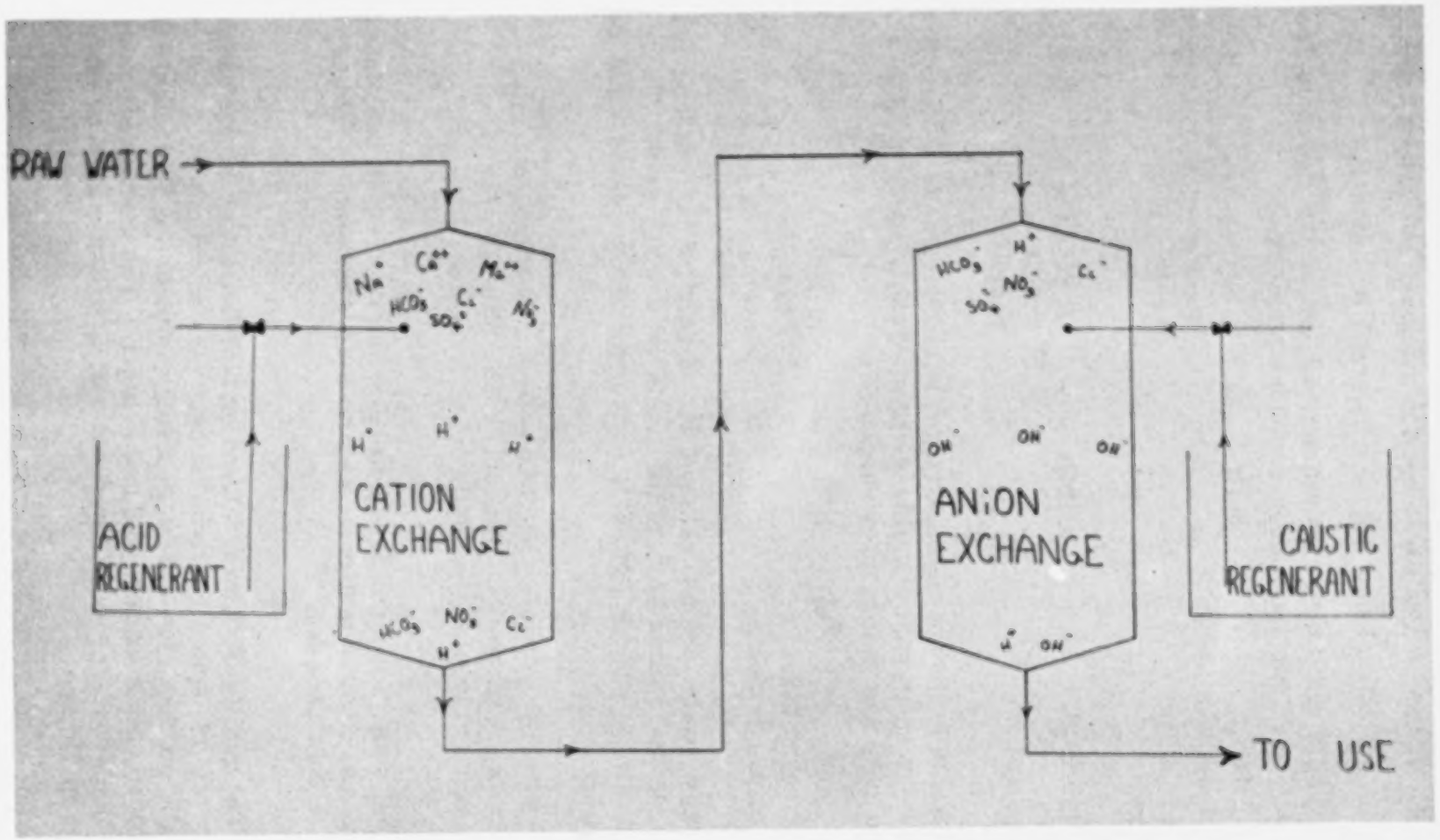


Figure 3: Schematic Illustration of Two-Bed Demineralization Process

DISSOLVED MINERALS

Minerals	Source	Potential Problems	Removal Methods
Iron (Fe^{+2}), (Fe^{+3}) Manganese (Mn^{+2}), (Mn^{+3})	Rocks and soils Corrosion of iron or steel surfaces	Depositions Staining Corrosion Growth of "iron or manganese" bacteria, which clog pipes and reduce flow rates	Aeration Coagulation and filtration Lime or limes - soda softening Cation exchange Contact filtration May be retained in solution by surface active agents
Sodium (Na^{+})	Rocks and soils	Foaming	Hydrogen ion exchange Demineralization Distillation
Alkalinity Bicarbonate (HCO_3^{-}) Carbonate ($CO_3^{=}$)	Rocks	Scale formation Foaming	Lime-soda softening Hydrogen ion exchange Sodium zeolite + chloride ion exchange
Chloride (Cl^{-})	Domestic wastes Industrial wastes Oil field brines	Corrosion	Demineralization
Sulfate ($SO_4^{=}$)	Soil Industrial wastes	Scale formation	Demineralization May be retained in solution by surface active agents
Silica (SiO_2)	Earth's crust	Formation of a hard scale	Highly basic anion exchange Demineralization

	Δ, μmhos
Calculated maximum quality of pure water	0.038
Single distilled water (glass apparatus)	2.0
Triple distilled water (glass)	1.0
Monobed demineralization	0.055
Twenty-eight distillations in quartz	0.044

Figure 4

The effectiveness of the various unit operations which have been discussed for removal of the hardness ions is compared in Figure 5.

Softening Process	Residual Hardness, mg/1
Cold lime-soda ash	30 - 50
Hot lime-soda ash (operated at temperatures near or above the boiling point)	15 - 25
Sodium zeolite	0 - 2
Sodium-Hydrogen zeolite	0 - 2
Demineralization	0 - 0.5

Figure 5

Iron and Manganese

Iron is present in raw water more often than manganese, but both may be found in either the oxidized or in the reduced state. They are usually present in rocks and soil in the oxidized form. When rain water percolates through the soil, decaying organic matter consumes the dissolved oxygen. Iron and manganese deposits are then reduced to soluble form and dissolved. These minerals are quite likely to be present in water drawn from the lower reaches of reservoirs, where dissolved oxygen is expected to be absent. The problems they cause and their treatment methods are similar.

Removal of iron (or manganese) by aeration involves two basic reactions:

1. Carbon dioxide is removed as a result of increasing the pH, and

2. Oxygen is added, chemically oxidizing the ferrous iron and precipitating ferric hydroxide.

Coagulation is usually achieved by the addition of alum (aluminum sulfate). In lime-soda softening, when the pH is raised sufficiently high for the softening reactions to proceed, iron is precipitated as ferric hydroxide.

With cation exchange, ferrous iron is exchanged either for sodium or for hydrogen ions, according to the following reaction:

$$Fe(HCO_3)_2 + \underset{\text{Sodium zeolite}}{Na_2Z} \longrightarrow \underset{\text{Ferrous zeolite}}{FeZ} + 2NaHCO_3$$

The usefulness of this method is limited to well waters. Iron must be in the ferrous state, therefore the water must not be aerated prior to treatment. Ferric hydroxide would cause fouling of the exchange resin.

Contact filtration may also be used to remove iron from water. There are essentially two types of contact filters. In one type, the filter bed contains manganese dioxide, which acts as a catalyst between the iron and the oxygen in the water. These are called "catalytic beds." In the other type, the filter bed itself supplies the oxygen. These must be regenerated periodically. Manganese zeolite is an example of this type.

Surface active agents—usually either polyphosphates or organic sequestrants—may be used to retain iron in solution. Either ferrous or ferric iron can be treated in this manner. (A brief discussion of this mode of action is included in the "detergent" section of this paper.)

Sodium

Sodium is found in nearly all natural waters. At high concentrations and at elevated temperatures, it may be a cause of foaming. It can be removed by hydrogen ion exchange, demineralization, or distillation.

Alkalinity

Alkalinity is generally considered to be due to bicarbonates (HCO_3^-), carbonates ($CO_3^=$), and hydroxide (OH^-), (although

other ions, such as phosphates and silicates may also be concerned). Natural waters usually contain only the bicarbonates.

Scale formation is the more serious problem associated with alkalinity. In general, the higher the alkalinity, the greater the tendency for precipitation of calcium carbonate scale. It is sometimes possible to predict this tendency for scaling by the use of Langelier's equation. This is an expression which relates the content of calcium and of alkalinity to certain other factors to determine the pH at equilibrium conditions. The arithmetic difference between the actual measured pH and the calculated equilibrium pH is an indication of the tendency to precipitate, or the tendency to dissolve.

Factors other than alkalinity which affect scale formation include temperature; the rate of heat transfer; the calcium, magnesium, sulfate, silica, and dissolved solids content of the water; and the pH of the water.

Alkalinity may also be responsible for foaming. It can be removed by lime-soda softening, hydrogen ion exchange, or by sodium zeolite followed by chloride ion exchange. The latter process differs from demineralization in that all ions are not removed from solution, but rather the undesirable ones are replaced by others of a more desirable character.

Chlorides

Domestic and industrial wastes and oil field brines contribute chlorides to water. Chlorides may cause corrosion. They can be removed by demineralization.

Sulfates

Sulfates enter water from the soil or from industrial wastes, particularly from acid mine drainage or waste pickle liquor. They can combine with calcium to form calcium sulfate scale. It is simpler and more economical to avoid this problem by removing the calcium; but sulfate can be removed by demineralization, or it can be retained in solution with surface active agents.

Chlorides, sulfates, and nitrates, when present with calcium or magnesium, form non-carbonate hardness.

Silca

Silica is dissolved by water from the earth's crust. It can form a very hard scale. Highly basic anion exchange and demineralization process will remove it.

DISSOLVED GASES

Oxygen

As rain water falls through the atmosphere, it picks up oxygen, nitrogen, and carbon dioxide in proportion to their partial pressures. Oxygen is also contributed by photosynthesis.

At low pH values, oxygen causes iron, steel, galvanized iron, and brass to corrode. The highest rate of corrosion occurs at 160-180^{O} F., a temperature which is very significant in the dishwashing industry. At a high pH, oxygen encourages the precipitation of calcium carbonate scale. Mechanical or chemical deaeration techniques can be used to remove oxygen from water.

DISSOLVED GASES

Gas	Source	Potential Problems	Removal Methods
Oxygen (O_2)	Atmosphere Photosynthesis	At low pH - Corrosion At high pH - Formation of scale	Mechanical or chemical deaeration
Carbon Dioxide (CO_2)	Decay of organic matter Rock and soils Atmosphere	Corrosion	Aeration Deaeration Neutralization Lime-soda softening
Hydrogen sulfide (H_2S)	Atmosphere Wells (sulfur waters)	Corrosion Odor problems In the presence of iron, black precipitate of FeS.	Aeration at low pH Chlorination Highly basic anion exchange
Ammonia (NH_3)	Decomposition of organic matter	Corrosion of copper and zinc and their alloys	Hydrogen ion exchange Break point chlorination

Carbon Dioxide

Decaying organic matter is the primary source of carbon dioxide in water, but it may also come from rocks or soil, or from the atmosphere.

Carbon dioxide is also a factor in corrosion.

Deaeration, neutralization, and lime-soda softening can remove CO_2 from water, but aeration is the technique most commonly used for this purpose. The fundamental principle involved when aeration is used to remove gases from water is the establishment of a state of equilibrium between the gases in the water and those in the atmosphere. This application follows Henry's Law, which states that the solubility of a gas in water is directly proportional to its partial pressure in the surrounding atmosphere.

Carbon dioxide is relatively soluble in water, but its partial pressure in the normal atmosphere is practically zero. The use of aeration to establish an equilibrium between water and air results in saturating the water with nitrogen and oxygen, releasing almost all the carbon dioxide from the water.

Hydrogen Sulfide

Hydrogen sulfide may be added to water from the atmosphere, but more often it is found in wells due to their location (near boulder clay areas, or "sour gas" oil fields), or to the presence of sulfur bacteria. It causes corrosion, has a typical "rotten egg" odor, and if iron is present, combines with it to precipitate black ferrous sulfide.

Aeration can also be used to remove hydrogen sulfide, but it must be carried out at a low pH. Chlorination is an effective—but expensive—way to remove it. (8 atoms of chlorine are required for the complete oxidation of 1 molecule of hydrogen sulfide:

$$H_2S + 4Cl_2 + 4H_2O \longrightarrow H_2SO_4 + 8HCl.)$$

Highly basic anion exchange can also be used.

$$(R_4N{\cdot}OH + H_2S \longrightarrow R_4N{\cdot}HS + H_2O)$$

Basic exchange resin — Sulfide resin

Ammonia

Ammonia is present in water as a result of the decomposition of organic matter. It corrodes copper and zinc and their alloys by the formation of a complex soluble ion. It can be removed by hydrogen ion exchange, or by breakpoint chlorination.

Chlorination

The chemistry of chlorination is briefly shown in the following series of reactions:

1. When chlorine is dissolved in water, it hydrolyzes rapidly to form hypochlorous acid and hydrochloric acid.

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$$

2. Hypochlorous acid will further dissociate to give hydrogen ions and hypochlorite ions:

$$HOCl \rightleftharpoons H^+ + OCl^-.$$

The relative proportions of molecularly dissolved chlorine, undissociated hypochlorous acid, and hypochlorite ions which exist in equilibrium vary with the pH as shown in Figure 6.

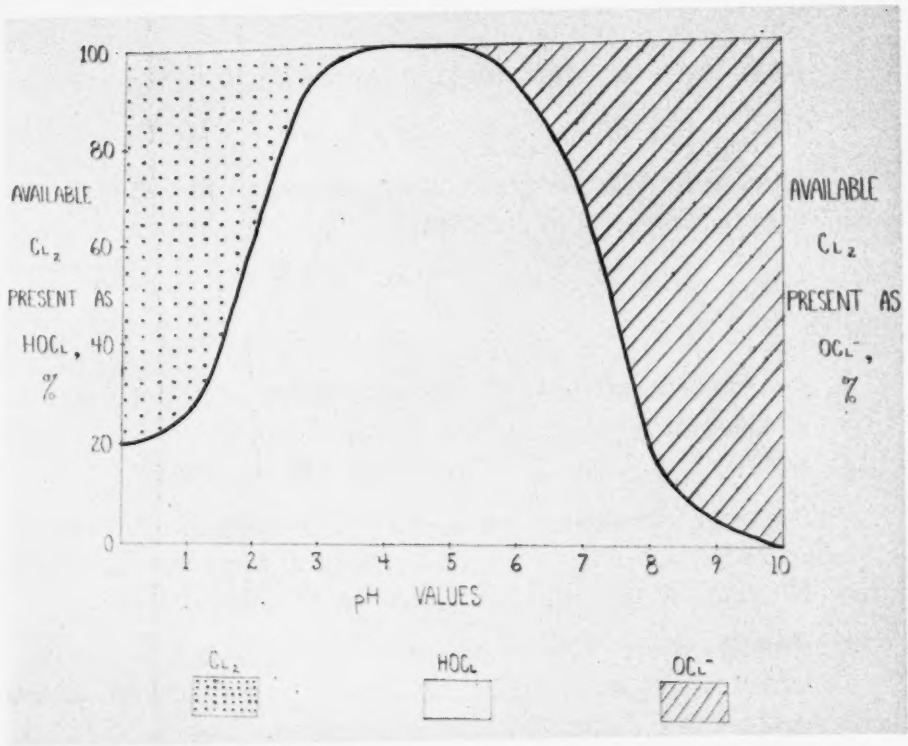


Figure 6

At pH values less than 3, molecularly dissolved chlorine is found. Between pH 4 and 5, chlorine exists almost entirely as unionized hypochlorous acid. Above pH 7.0, hypochlorite ion becomes significant. Unionized hypochlorous acid and hypochlorite ions are present in equal proportions only at pH 7.4.

These reactions are the same whether the chlorine is introduced as chlorine gas or as a hypochlorite.

At this point it is important to define a few terms.

1. *Free Available Chlorine* is chlorine in the elemental form, as hypochlorous acid, or as hypochlorite ions, or a mixture of these in any proportions.
2. *Combined Available Chlorine* is chlorine which has combined with ammonia or with other nitrogenous compounds to form chloramines.
3. *Chlorine Demand* is that amount of chlorine required to react in a given time with the impurities present, so that any further addition of chlorine will give a free residual. For example: If Fe^{++}, Mn^{++}, NO_2^-, or H_2S are present, they will be oxidized by chlorine, and the chlorine will be reduced to chloride ions. Chloride ions have no disinfecting capacity.

   $$H_2S + 4Cl_2 + 4H_2O \longrightarrow H_2SO_4 + 8HCl.$$

   Also certain organic compounds, like phenol, for example, may react directly with chlorine:

   $$Cl_2 + \text{Phenols} \longrightarrow \text{Chlorophenols} \downarrow \text{Taste and odor problems}$$

4. *Superchlorination* is the practice of adding chlorine greatly in excess of the immediate demand in order to achieve a high chlorine residual at once.

   Superchlorination is used when complete sterilization is required but very little contact time is available. It is almost always followed by dechlorination.

5. *Break-point Chlorination* is the technique in which chlorine is applied beyond the point where complete oxidation of chloramines has occurred, so that further addition of chlorine will provide a free residual.

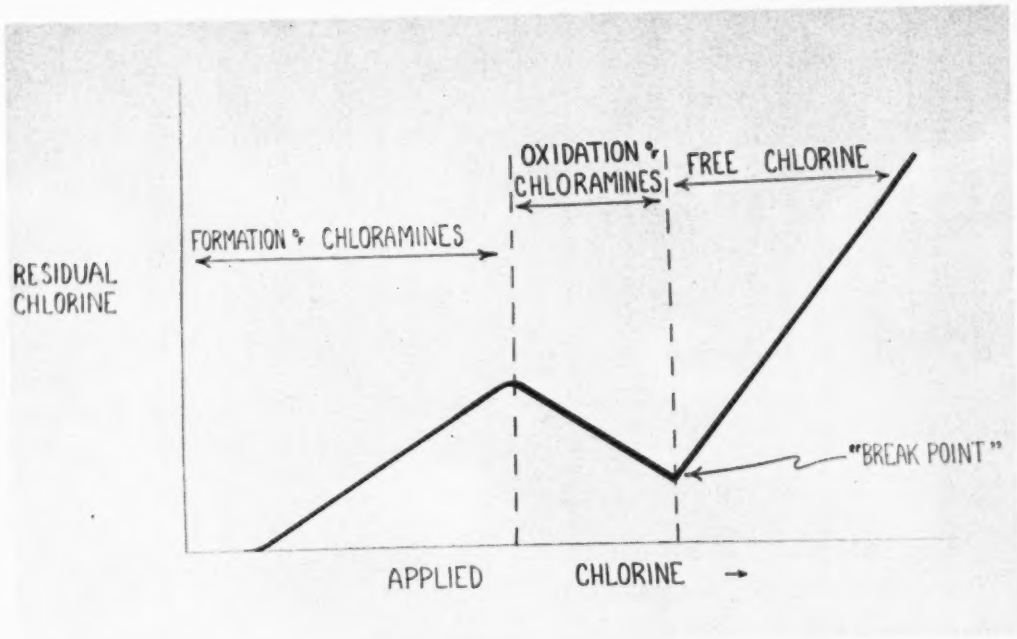


Figure 7: A Typical Curve For Breakpoint Chlorination

Most raw waters contain nitrogenous compounds as impurities, so the addition of chlorine can first be expected to form chloramines:

$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$
Monochloramine

$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$
Dichloramine

$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$
Nitrogen trichloride

$NH_2Cl + NH_2Cl \longrightarrow N_2 + 3HCl.$

$2NH_3 + 3HOCl \longrightarrow N_2 + 3HCl + 3H_2O$

These reactions vary with pH and with ammonia/chlorine ratio.

Factors which affect the action of chlorine include:

1. pH
   Hypochlorous acid is the form which has the greatest capacity to disinfect.

OTHER IMPURITIES

Impurity	Source	Potential Problems	Removal Method
Free mineral acid acidity	Industrial wastes	Corrosion	Neutralization
Oils and greases	Domestic wastes Industrial wastes	Films Foaming Formation of sludges	Coagulation and filtration Diatomaceous earth filters
Turbidity and suspended solids	Land erosion Domestic wastes Industrial wastes	Sedimentation Foaming	Coagulation and filtration Lime-soda softening
Color and organic matter	Farm runoff Domestic wastes Industrial wastes Flooding of swamps	Foaming Staining	Coagulation at low pH and filtration Activated carbon adsorption Chlorination
Tastes and odors	Algae and other living microorganisms Domestic wastes Industrial wastes		Break-point chlorination Aeration Activated carbon adsorption
Microorganisms	Domestic wastes Farm runoff Flooding of swamps	Formation of slimes, which cause fouling of unit operations and corrosion	Chlorination Coagulation and filtration

2. Temperature
   The rate of disinfection increases with increased temperature.

3. Concentration

4. The form in which chlorine is used.
   Free chlorine, applied either as chlorine gas or as a hypochlorite, is a much more rapid disinfecting agent than chloramine, if organic matter and reduced inorganic compounds are absent. Chloramines may be a more effective agent, however, if these substances are present, for it reacts only slightly with some and not at all with others. In order to effect a "complete" kill, a contact period up to 100 times longer is required with the use of chloramines.

Free Mineral Acids

Free mineral acids may be present in water as a result of the discharge of industrial wastes, particularly acid mine drainage or waste pickle liquor. They are a direct cause of corrosion. They can be removed by neutralization with lime, caustic soda, or soda ash.

Oils and Greases

Domestic and industrial wastes contribute oils and greases to water supplies. These contaminants may cause the formation of film, foam, or sludge.

Coagulation

Suspended solids, turbidity, color, and microorganisms are removed by coagulation. This is the process by which finely divided particles are agglomerated into larger masses, in order to effect more rapid settling. Aluminum sulfate—alum—is the coagulant most commonly used in water conditioning. Others include ferrous sulfate — copperas — and the ferric coagulants — ferric sulfate and ferric chloride.

Polyelectrolyte coagulant aids are becoming more and more popular. These are high molecular weight, water soluble polymers which can dissociate to yield highly charged, large molecular weight ions. They may be anionic, cationic, or nonionic.

DETERGENTS

By definition, a "detergent" is a "cleaning agent," therefore, any compound used for cleaning purposes—soaps, synthetic powders and liquids, solvents, and even abrasives such as sand—are "detergents." In popular usage, however, the term generally refers to packaged cleaners used for laundering, dishwashing, etc.—products which have soapy characteristics without having the disadvantages commonly found with a true soap in hard water. Soap is a sodium or potassium salt of a long chain organic acid. Its structure is typical of that shown in Figure 8.

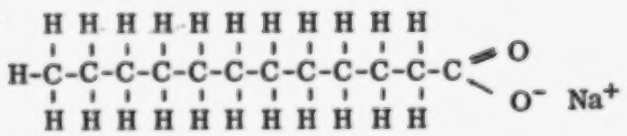


Figure 8: Structure of a Typical Soap

Under acid conditions, or in hard water, the detergent properties of soap are destroyed. Soap forms a curd with the hardness ions, resulting in undesirable precipitates and considerable waste of soap. (1-1/2 pounds of pure soap are destroyed per 100 gallons of water per grain of hardness.)

Detergents are formulated from a number of different compounds. These include:

*1. Alkalies

Which may: (1) Soften the water (by precipitation of the hardness ions)
**(2) Saponify fats

2. Complex phosphates

Which may: (1) Emulsify fats and oils
(2) Disperse and suspend them
(3) Peptize proteins
(4) Soften the water (by sequestering)
and (5) Provide rinseability characteristics without being corrosive.

*, ** Lists of compounds and definitions are appended.

3. Organic compounds

   a. Chelating agents
      Which
         (1) Soften the water (by sequestering)
         (2) Prevent mineral deposits
      and (3) Peptize proteins without being corrosive.

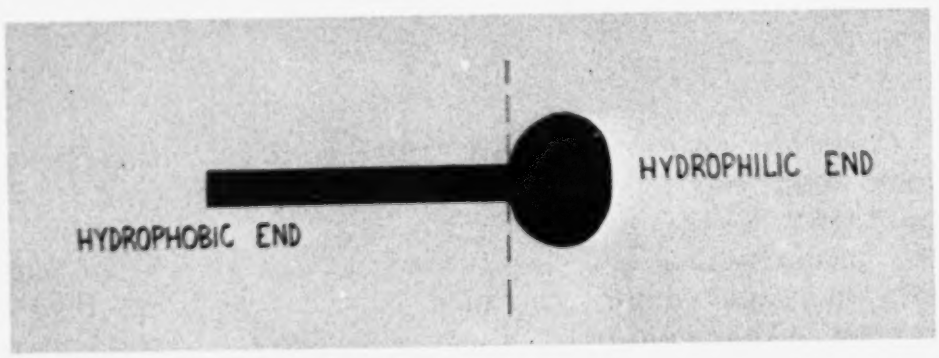
   b. Wetting agents
      Which:
         (1) Emulsify fats
         (2) Disperse them
         (3) Provide wetting properties
         (4) Can form suds
      and (5) Provide rinseability without being corrosive.

   c. Organic acids
      Which:
         (1) Prevent mineral deposits (by sequestering)
      and (2) Soften the water without being corrosive

4. Mineral acids
   Which:
      (1) Prevent mineral deposits
   and (2) Soften the water.

Detergents are classified as anionic, cationic, nonionic, or amphoteric, according to the way they ionize in solution. The anionics are by far the most widely used.

Very basically, an anionic surfactant molecule (the active portion of a formulated detergent) can be visualized as consisting of two parts, a "head" and a "tail."



Surfactant Molecule

Chemically, the "tail" is the active part of the molecule. It consists of the long chain hydrocarbon portion, which is hydrophobic, or "water-hating." The "head" is the sodium portion. It is hydrophilic, or "water-loving." These molecules gather together in rather well-defined aggregates called "micelles." When foreign matter—soil, for example—is present, it is taken into the micelle and suspended in the solution. Excess surfactant molecules migrate to the air-water interface where they form suds, or, in the case of the now notorious waste treatment plants, they form aesthetically objectionable "foam."

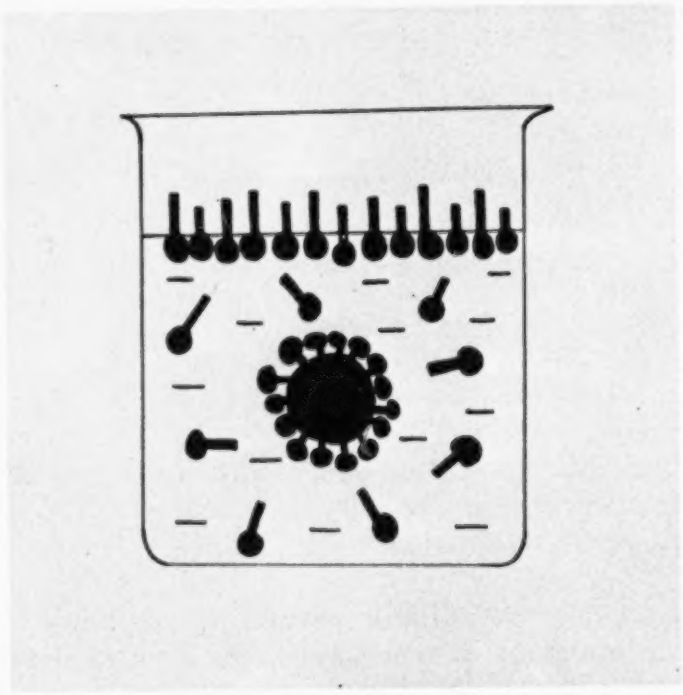
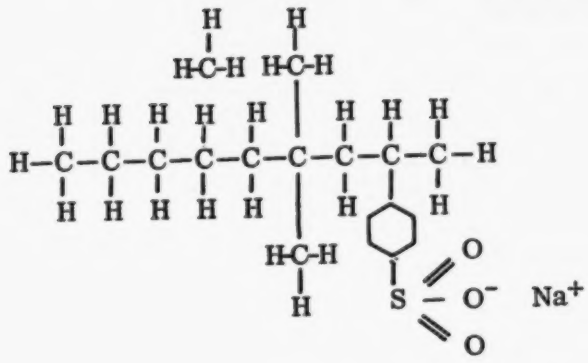
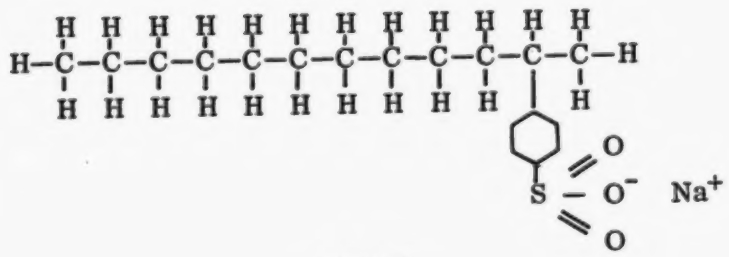


Figure 9: Schematic Illustration of Soil Suspension by Micelle Formation

Certainly everyone is aware of the recent changeover in anionic detergents from the branched-chain, slowly biodegradable "ABS" to the linear, readily biodegradable "LAS." No other industry has ever responded so completely to public apathy—perhaps public ignorance is a better term—than the detergent industry did in effecting this change. Typical structures of ABS and LAS are shown in Figure 10.



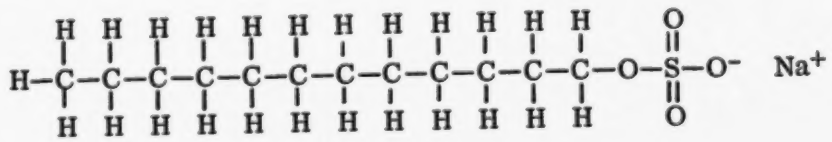
"ABS"



"LAS"

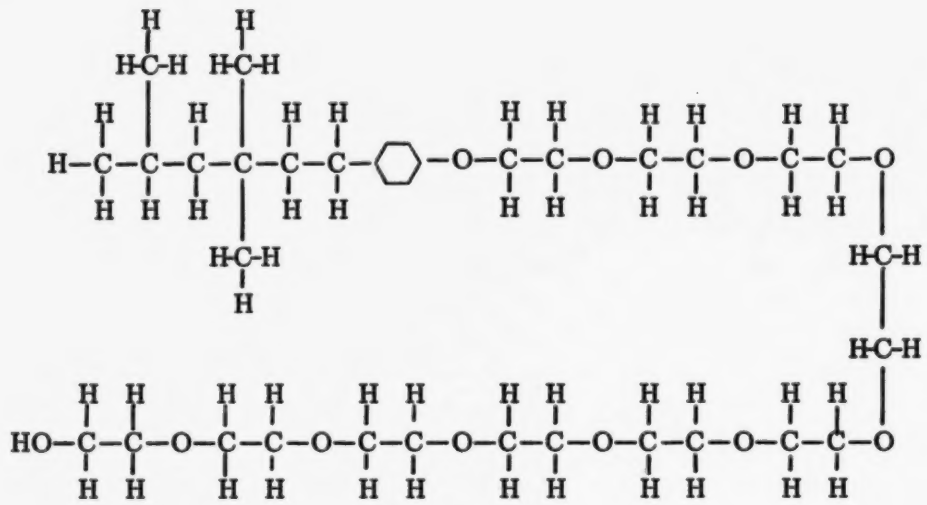
Figure 10

Both of these compounds are petroleum-derived surfactants. The third structure is that of alkyl sulfate, an alcohol derivative which is the next most popular of the anionics.



Alkyl Sulfate

Nonionic surfactants do not ionize in solution. This type of surfactant is gaining rapidly in popularity. Contrary to popular belief, the nonionics are not all rapidly biodegradable. If they were used in the quantities that ABS was, they could cause just as much controversy.



Alkylphenol Ethoxylate

The cationics contain a positively charged hydrophobic group. The quaternary ammonium compounds, which are sometimes used as sanitizing agents, belong to this group. These are fairly effective germicides, but they are generally not good cleaners. They are sometimes used in preference to chlorine in rinse solutions.

The cationics are non-irritating, and they offer prolonged bacteriostatic action, but they also have a number of limitations:

1. They're expensive
2. Their mechanism of action is slow,

and 3. They may be inhibited by the hardness ions, or by incompatible detergents (anionics) used in the cleaning operation.

If the quaternary ammonium compounds are used as cleaners, their formulation must include an efficient, compatible detergent, and a sequestering agent to nullify the adverse effect of any hardness ions which may be present.

Industrial water conditioning simply involves fitting water to the job. The U.S. Public Health Service Drinking Water

Standards establish minimum standards for drinking water quality. No similar standards can be formulated for industrial supplies because of the tremendous difference in needs. It is impossible to define industrial water "quality" criteria in general terms, just as it's impossible to define what constitutes an economically feasible industrial treatment method. Each is relative and must be considered on an individual basis.

Rates for water purchased from public and private utilities vary considerably across the country, but the national average is 35¢ per thousand gallons, or about 2¢ per person per day. Most major industrial self-supplied water used in substantial quantities can be pumped, treated, and distributed for 1 to 15¢ per thousand gallons. (This varies, of course, with the degree of treatment required.) Based on these figures, would you consider the water the U.S. Navy shipped into Guantanamo Bay during the recent Cuban crisis at a cost of $8 per thousand gallons "economically feasible"? Or the bottled spring water purchased by the residents of Chanute, Kansas during their severe drought in 1956 . . . This cost $3.50 per five gallon jug, or $700 per thousand gallons... Was this "economically feasible"? Certainly "need" is the primary consideration.

The question of predicting future water demands will also probably be raised. Perhaps this is possible for domestic usage, but it doesn't seem reasonable to venture a guess where industry is concerned. Major industrial users in 1980 may well be concerned with the manufacture of products which we haven't yet even dreamed of.

In summary, a number of the chemical and physical factors which can cause dishwashing problems are presented in the following chart. Water quality considerations are vital, but the importance of good housekeeping and proper operating practices cannot and must not be minimized.

SUMMARY OF CHEMICAL AND PHYSICAL FACTORS WHICH CAN CAUSE DISHWASHING PROBLEMS

Symptom	Possible Cause	Suggested Cure
Films	Water hardness	Use an external softening process Use more detergent to provide internal conditioning Use a chlorinated cleaner Check temperature of wash and rinse water Overheated water may be precipitating film
	Detergent carry-over	Maintain adequate pressure and volume of rinse water
	Improperly cleaned or rinsed equipment	Prevent scale build-up in equipment by adopting frequent and adequate cleaning practices. Maintain adequate pressure and volume of rinse water.
Greasy films	Low pH Insufficient detergent Low water temperature	Maintain adequate alkalinity to saponify greases.
	Improperly cleaned equipment	Unclog all wash sprays and rinse nozzles to keep any greases carried in the steam from depositing on dishes. Clogged rinse nozzles will also interfere with wash tank overflow, allowing surface scums to remain in the machine.
Streaking	Alkalinity in the water	Use an external treatment method to reduce alkalinity.
	Improperly cleaned or rinsed equipment	Maintain adequate pressure and volume of rinse water. Alkaline cleaners used for washing must be thoroughly rinsed from dishes.
Spotting	Rinse water hardness	Provide external or internal softening.
	Rinse water temperature too high or too low	Check rinse water temperature. Dishes may be flash drying, or water may be drying on dishes rather than draining off.
	Inadequate time between rinsing and storage	Allow sufficient time for air drying.

	Inadequate time between rinsing and storage	Allow sufficient time for air drying.
Staining	Iron in water	Check for corrosion Retain iron in solution with surface active agents.
	Color in water	Provide external treatment for iron or color removal.
Foaming	Detergent	Change to a low sudsing product.
	Dissolved or suspended solids in water	Use an appropriate treatment method to reduce the solid content of the water.
	Food soil	Adequately remove gross soil before washing. The decomposition of carbohydrates, proteins, or fats may cause foaming during the wash cycle.
	Alkalinity, oils, or color in water supply	Use an appropriate treatment method to reduce or remove these factors.
	Improperly cleaned equipment	Keep all wash sprays and rinse nozzles open. Keep equipment free from deposits or films of materials which could cause foam build-up in future wash cycles.
Dirty dishes	Insufficient detergents	Use enough detergent in wash water to insure complete soil suspension.
	Wash water temperature too low.	Keep water temperature high enough to dissolve food residues.
	Inadequate wash and rinse times.	Allow sufficient time for wash and rinse operations to be effective.
	Improperly cleaned equipment	Unclog wash sprays and rinse nozzles to maintain proper pressure and flow conditions. Overflows must be open. Keep wash water as clean as possible

Appendix 1: Compounds used in Detergent Formulations

Alkalies:

Caustic soda	($NaOH$)
Sodium metasilicate	($NaSiO_3$)
Soda ash	(Na_2CO_3)
Trisodium phosphate	(Na_3PO_4)

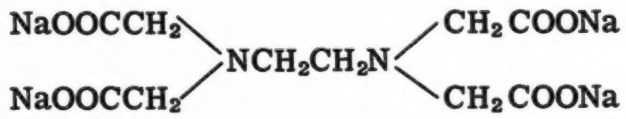
Complex phosphates:

Sodium tetraphosphate	($Na_6P_4O_{13}$)
Sodium tri-polyphosphate	($Na_5P_3O_{10}$)
Sodium hexametaphosphate	($(NaPO_3)_6$)
Tetrasodium pyrophosphate	($Na_4P_2O_7$)

Organic compounds:

Chelating agents:

Sodium salts of EDTA (ethylenediaminetetraacetic acid)



Tetrasodium EDTA

Certain other organic acid salts

Wetting agents:

Anionic, nonionic, or cationic surface active agents.

Organic acids:

Gluconic acid	($C_5H_6(OH)_5COOH$)
Hydroxyacetic acid	($HOCH_2COOH$)
Citric acid	($COOHCH_2COHCOOHCH_2COOH$)

Mineral acids:

Hydrochloric acid	(HCl)
Sulfuric acid	(H_2SO_4)
Sodium acid sulfate	($NaHSO_4$)
Sulfamic acid	(HSO_3NH_2)
Nitric acid	(HNO_3)
Phosphoric acid	(H_3PO_4)

Appendix 2: Definitions

Saponification—
The chemical reaction between an alkali and a fat in which soap is produced.

Emulsification—
The physical action in which fats are mechanically broken up into very small particles which are uniformly suspended in a solution.

Sequestering Agents—
Compounds which will react with certain ions to form relatively stable, water soluble complexes. Polyphosphates are often used in detergent formulations to prevent precipitation of the hardness ions by this action.

Chelating Agents—
Organic sequestering agents.

Wetting Agents—
Compounds which reduce surface tension, increasing the capacity of water for contacting all liquid-surface areas.